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DEVELOPMENT AND OPTIMIZATION OF FLOW-CAST MAGNESIUM FLARE COMPOSITIONS

THE DOW CHEMICAL COMPANY

TECHNICAL REPORT AFATL-TR-72-105

JUNE 1972

AIR FORCE ARMAMENT LABORATORY
AIR FORCE SYSTEMS COMMAND • UNITED STATES AIR FORCE
EGLIN AIR FORCE BASE, FLORIDA

Development And Optimization Of Flow-Cast Magnesium Flare Compositions

George A. Lane
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Keith Roberson

FOREWORD

This report covers work performed during the period 21 April 1971 to 14 February 1972 by the Dow Chemical Company, Midland, Michigan, under Contract F08635-71-C-0120, "Development Program for Optimizing Flow-Cast Flares", with the Air Force Armament Laboratory, Eglin Air Force Base, Florida. Captain Robert Dowrie (DLIP) was program monitor for the Armament Laboratory.

Management direction at The Dow Chemical Company was under Dr. E. T. Niles, and technical supervision under Dr. G. A. Lane. Major contributions were made by Erwin M. Jankowiak and Keith Roberson.

This technical report has been reviewed and is approved.

FRANKLIN C. DAVIES, Colonel, USAF
Chief, Flame, Incendiary, and Explosives Division

ABSTRACT

Previous work (Contract F08635-70-C-0028, Eglin Air Force Base) gave encouraging results for flow-cast illumination flares. The present development effort has resulted in compositions comparable in performance with pressed mixtures. Viton®-lined paper phenolic cases have proved satisfactory in 3.4-inch-diameter size. The agglomeration of sodium nitrate can be reduced by the addition of MgO and Cab-O-sil. However, the oxidizer also should be used immediately after grinding to avoid agglomeration. Surfactants can be used to improve mix viscosity. The particle size distribution of magnesium used is critical to mix viscosity and luminous efficiency. With 20 percent binder in the mix, maximum performance is obtained at about 52 percent Mg for 1.25-inch candles and 50 percent Mg for 3.4-inch candles. The best efforts formulation contains 50 percent of a 40/200 mesh Mg blend, 30 percent $NaNO_3$, and 20 percent of XFS-4008L - EC-MA - DEGDN binder. In 3.4-inch candles it yields 43 to 45,000 cd-sec/g efficiency at 0.056-0.059 in./sec. burning rate. This mix has been scaled up to 10-kg batch size. Further work has also been accomplished on new binders. The most promising is based on a vinyl ester, Tex-R-1939, plasticized with DEGDN.

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GLOSSARY

ADGC - allyl diglycol carbonate.
AGE - allyl glycidyl ether.
AOPG - allyloxypropyl glycidyl ether.
DEGDN - diethylene glycol dinitrate.
D.E.H.® 20[1] - diethylenetriamine.
DETA - diethylene triamine.
EC - ethylene carbonate.
EC-MA - 1:1 solution of ethylene carbonate and maleic anhydride.
EDA - ethylene diamine.
HEA - hydroxyethyl acrylate.
MA - maleic anhydride.
MEK - methyl ethyl ketone.
PGNC - plastisol grade nitrocellulose.
TEA - triethanolamine.
TEGDN - triethylene glycol dinitrate.
XF-4013L - sulfur - containing epoxy resin.
XFS-4008L - glycerine diglycidyl ether.

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[1]D.E.H., a trademark of The Dow Chemical Company for epoxy curing agent.

SOURCES OF MATERIALS

ADGC - PPG Industries
AGE - Alcolac, Incorporated
AOPG - The Dow Chemical Company
Cab-o-sil M-S - Johns Manville Company
Cumene Hydroperoxide - Hercules, Incorporated
Crystal Bay Tape - 3M Company
DEGDN - Commercial Solvents Corporation
D.E.H.® 20 - The Dow Chemical Company
DETA - The Dow Chemical Company
Diethyloxalate - Eastman Kodak Company
Dowanol EM - The Dow Chemical Company
EC - Jefferson Chemical Company
EDA - Eastman Kodak Company
Ethylene Glycol - The Dow Chemical Company
HEA - The Dow Chemical Company
Lauroyl Peroxide - Chemtron Noury Corporation
MA - Matheson, Coleman and Bell Company
Magnesium, Atomized - Valley Metallurgical Products Company
Magnesium Oxide - Allied Chemical Company
MEK Peroxide - Pennwalt Corporation
Mylar® Film - E. I. Dupont de Nemours and Company
PGNC - E. I. Dupont de Nemours and Company
Potassium Chlorate - American Potash and Chemical Company
Sodium Nitrate - Davies Nitrate Company
Sprayon Paint - Sprayon Products, Inc.
Tartaric Acid - J. T. Baker Chemical Company
TEA - The Dow Chemical Company
TEGDN - Propellex
Tergitol E-35 - Union Carbide Corporation
Tex-R-1939 - The Dow Chemical Company
Viton® - E. I. Dupont de Nemours and Company
XF-4013L - The Dow Chemical Company
XFS-4008L - The Dow Chemical Company

SECTION I

INTRODUCTION

The objectives of this effort were to optimize the best efforts castable magnesium-sodium nitrate flare composition developed under Contract No. F08635-70-C-0028, "Flow Cast Flare Composition," and to develop new compositions based on new binders.

The best efforts formula from the previous contract contained 22% binder, consisting of 25% XFS-4008L, 35% EC-MA (ethylene carbonate-maleic anhydride in a 1-1 ratio), and 40% DEGDN (diethylene glycol dinitrate). The total composition contained:

52%	Magnesium, 40/200 mesh
26%	$NaNO_3$, <400 mesh
5.5%	XFS-4008L
7.7%	EC-MA
8.8%	DEGDN

The basic characteristics were:

Viscosity at 25°C - 563,000 cps
Luminous Efficiency - 70,000 cd-sec/g
Burning Rate - 0.056 in./sec.
Grain Integrity and Surveillance
Stability - Acceptable

In order to compare light output and efficiency with known flare compositions, pressed candles containing the composition used in Mark 45 flares were fired at frequent intervals in conjunction with firings of the developmental flares. The best efforts flow cast composition was expected to give about 5,000 cd-sec/g less luminous efficiency than the pressed Mark 45 composition at approximately the same burning rate.

The present effort was directed at investigating the various parameters that might contribute to a reduction in binder level and improvement in light output without sacrificing the physical and stability properties of the best efforts flare composition. This work also included restandardization of light measuring equipment, investigation of inverted flare firings, adapting for the use of 3.4 inches ID paper-phenolic cases, studying $NaNO_3$ particle size and dispersion, and investigating magnesium particle size distribution.

A second objective was to continue development of new and improved binder systems for flow-cast magnesium-$NaNO_3$ illuminating flares.

SECTION II

PROCEDURES

The following experimental conditions were used, unless specified otherwise in the report:

1. Sodium nitrate - Powdered Davies $NaNO_3$, containing 0.50 percent MgO and 0.25 percent Cab-o-sil, was ground in a Mikro-Pulverizer and dried at least 16 hours at 80°C.

2. Magnesium - atomized 40/200 mesh Valley Metallurgical Mg powder was used. The work reported was done with different batches of 40/200 mesh material (see page 14 for mesh analyses).

3. TEGDN or DEGDN - No inhibitor.

4. Mixing - All work was done with a KitchenAid model K5-A mixer, wire whip blade at minimum speed. The following procedure was adopted: Add epoxy resin, curing agent and plasticizer; mix 1 to 2 minutes; add $NaNO_3$; mix 5 to 10 minutes; add Mg; mix for 10 to 15 minutes. Batches of 420 to 8000 g were prepared.

5. Fluidity - The viscosity was determined on an aliquot sample of the mix at 25°C using Brookfield RVF viscometer with T-type spindle.

6. Casting - The composition was poured into a 6-inch plastic funnel, and allowed to flow into a mold or flare case. Four to six candles (100 or 1200 g) were prepared per batch.

7. Mold - For the tape-wrapped candles a 1-1/4 inch I.D. by 4-inch long cardboard tube was lined with Mylar® film and plugged at the bottom with a No. 7 neoprene stopper. The mold was filled to a depth of 3.4 to 3.5 inches. When a case was used, the mix was poured directly into the prepared flare case.

8. Curing - Candles were cured at 70°C for 16 to 40 hours, depending on circumstances .

9. Tape Wrapping - The cured candle was removed from the mold, weighed and measured, reinserted into the mold, and an epoxy-sand plug was cast and cured at 20°C on the top (uppermost during casting) surface. Candles were removed from the mold, sprayed with Sprayon No. 321 paint for case-bonding and spirally wrapped (bifilarly) with Crystal Bay (2-inch width) masking tape. About 1 inch extra case was left at the top for the igniter. A very small overlap of tape was used, resulting essentially in a 2-ply case.

10. Density - Density was determined geometrically from the weight and measured size of the candle.

11. Igniter - The following composition was mixed, cast, and cured as a 0.5-g igniter pellet, attached to a length of igniter cord.

11.8%	Mg, 100/200 mesh
54.0%	$KClO_3$, Class 7
19.8%	XF-4013L
12.6%	MA
1.8%	Nitrocellulose powder

12. Attitude - The 1 1/4-inch candles were burned vertically, ignited on the upper surface. Air flow was upward. The 3.4-inch candles were tested both in this position and inverted.

13. Flare Tunnel - The flares were fired in an 18-foot 8-inch deep by 10-foot 5-inch wide by 10-foot 4-inch high concrete block hearth. The bottom of the flare was 4 feet 9 inches above the floor. Ventilation was accomplsihed by an inlet in the floor below the flare and an external 2-speed blower above the flare in the roof. The flare tunnel itself, connected to the hearth by a 4-foot by 9-foot doorway, is 60 feet long by 10 feet 5 inches wide by 14 feet high. The interior of the hearth and tunnel are painted black.

14. Light Measurement - Two Model 856 YYV Weston selenium photovoltaic cells are positioned 51.95 feet and 62.57 feet from the flare, at heights above the floor of 5.1 and 5.5 feet. The outputs of the photocells are amplified by Honeywell Accudata 120 amplifiers. Light output is recorded on a Honeywell Model 906B Visicorder oscillograph. A Dymec Model 2210 voltage-to-frequency converter and a Hewlett Packard Model 523 CR electronic counter are used to integrate the light output and record the integrated luminosity.

The photocell is standardized with a General Electric Lamp No. 1M/T20BP, which at a constant amperage yields a specific horizontal candle-power.

15. Burning Time - Time of functioning was determined visually with a stop watch.

16. Replications - At least four candles were fired for each data point.

SECTION III

CASE STUDY

A. PAPER-PHENOLIC CASES (1.25-INCH DIAMETER)

It was desired that optimization be conducted on compositions encased in 3.4-inch paper-phenolic tubing. Initial studies were conducted in 1.25-inch diameter paper-phenolic cases to determine the compatibility and case bonding properties of this composition with the case material. As shown in Table I, initial tests showed a failure in case bonding, as indicated by marked increase in combustion rate and reduction in luminous efficiency. Lining paper-phenolic cases with Viton® lacquer (3,000 to 3,500 cps, acetone-Viton® solution) gave enough improvement to warrant an immediate investigation of Viton®-lined paper-phenolic cases of 3.4-inch diameter.

TABLE I. COMBUSTION BEHAVIOR OF CANDLES IN PAPER-PHENOLIC TUBES

	Cast Composition[a]			Mark 45 Composition
	1.25-inch Paper-Phenolic			
	Unlined	Viton®-Lined	Paper-Tape	Paper Tape
Burn Rate in/sec	0.086	0.046	0.055	0.063
Efficiency cd-sec/g	24,000	39,200	49,800	57,300
Flame	Split	Smooth Straight	Smooth Flared	Smooth Straight
Chimney	Large	Small	None	V. Slight

[a] 50.29 percent magnesium, 27.71 percent $NaNO_3$, 5.96 percent XFS-4008L, 8.04 percent EC-MA, 7.70 percent DEGDN.

B. PAPER-PHENOLIC CASES (3.4-INCH DIAMETER)

Initial investigation yielded consistently low luminous efficiencies for 3.4-inch candles in Viton®-lined paper-phenolic cases, when fired in either the upright or inverted position. This was attributed primarily to chimney effects. However, smoke obscuration also was evident in the inverted

firings. The data in Table II indicate good case bonding with the 0.110-inch wall cases. Attempts were made to overcome the chimney effect and improve luminous efficiency by (1) reducing wall thickness from 0.110 inch to 0.055 inch and (2) using cases with 1/2-inch alternating bands of 0.110-inch and 0.056-inch thickness or 0.077-inch and 0.056-inch thickness. As may be seen in Table II, good case bonding and higher luminous efficiencies were achieved in some tests. However, because the 0.055-inch wall proved unacceptable, and the 0.077-inch wall was unpredictable, further work was done on flare preparation procedures. This showed that modifications in casting and case-bonding procedures resulted in acceptable combustion behavior for the 0.110-inch wall 3.4-inch I.D. paper-phenolic cases. These data are shown in Table III.

Good combustion results were obtained by using a thinner Viton lining (2,500 to 2,700 lacquer viscosity), and by bonding the epoxy-sand plug to the flare base. Efficiencies comparable to the ribbed case and approaching the results with 2-ply paper tape were obtained. This type of case and method of flare preparation were adopted for optimization purposes.

C. FISH PAPER AND COTTON-PHENOLIC CASES

Data are presented in Table IV for 1.75-inch diameter fish-paper cases. The thicker 1/16-inch wall cases give the best results in the inverted position. Flare composition XFS-4008L - EC-MA - DEGDN) cast in these Viton® lined cases displays a luminous efficiency and burning rate equivalent to the 2-ply paper-tape wrapped case. Interestingly, lining of the fish-paper cases with Viton® is detrimental in the thinner 1/32-inch wall cases. This strongly suggests that Viton® contributes to case bond failure during functioning in this case. The 1/16-inch wall thickness appears practical for either lined or unlined cases.

Cotton-phenolic cases were tested (0.075-inch wall) and displayed good case-bonding, as indicated by the burning rate 0.055 in/sec. However, luminous efficiency, 20,000 cd-sec/g, was surprisingly low, considering there was no residual chimney.

Thus, the preferred 1.75-inch diameter case appears to be 1/16-inch wall fish-paper, followed closely by the Viton® lined paper-phenolic. Fish-paper cases need to be investigated for 3.4-inch diameter candles.

TABLE II. STUDY OF 3.4-INCH DIAMETER FLARES[a]

Number of Firings	Case	Case Wall (inch)	Flare Attitude	Burn Rate (in/sec)	Luminous Efficiency (cd-sec/g)
2	Viton®-lined paper phenolic	0.110	Upright	0.057	30,600
2[b]	Viton®-lined paper phenolic	0.110	Inverted	0.056	27,800
1	Viton®-lined paper phenolic	0.077	Inverted	0.063	46,700
1	Viton®-lined paper phenolic	0.077	Inverted	0.132	27,800
1	Viton®-lined paper phenolic	0.077	Inverted	0.105	21,800
1	Viton®-lined paper phenolic	0.077	Inverted	0.106	23,200
2	Viton®-lined paper phenolic	0.055	Upright	0.122	27,400
2	Viton®-lined paper phenolic	0.055	Inverted	0.138	24,800
1	Viton®-lined paper phenolic	0.077-0.056[c]	Inverted	0.074	45,200
1	Viton®-lined paper phenolic	0.110-0.056[c]	Inverted	0.057	43,400
2	2-ply paper tape	---	Upright	0.052	51,400

[a]Composition 52/26/22 - Mg/$NaNO_3$/XFS-4008L - EC-MA - DEGDN.

[b]Flare and case fell during functioning of one flare. Data based on single flare.

[c]Banded case, alternating 1/2-inch segments of different thickness.

TABLE III. EFFECT OF PREPARATION METHOD OF 3.4-INCH DIAMETER FLARES

Composition(%)[b]			Case	Case Wall (inch)	Viton® Lining	Burn Rate (in/sec)	Luminous Efficiency[a] (cd-sec/g)
Mg	$NaNO_3$	Binder					
52	26	22	Unbonded sand plug[c,d]	0.110	Heavy[e]	0.056	27,800
52	26	22	Bonded sand plug[c]	0.110-0.056 Banded	Thin[f]	0.055	43,400
52	28	20	Bonded sand plug[c]	0.110	Thin	0.061	42,600
50	30	20	Bonded sand plug[c]	0.110	Thin	0.059	45,000
52	26	22	2-Ply paper tape	--	--	0.052[g]	51,400[g]

[a] Inverted firings.

[b] XFS-4008L - EC-MA - DEGDN.

[c] Paper phenolic case.

[d] Dow Corning release agent between sand plug and flare base.

[e] Initial Viton® linings not measured but estimated at significantly thickner than 0.0035 inch.

[f] Measured to be 0.0035-inch thick.

[g] Upright firing.

TABLE IV. STUDY OF 1.75-INCH FLARES IN FISH-PAPER CASES[a]

Number of Firings	Case	Wall Thickness (inch)	Flare Position	Length (inch)	Density (g/cc)	Weight (g)	Burn Rate (in/sec)	Luminous Efficiency (cd-sec/g)
4	Viton®-lined fish-paper	1/16	Inverted	3.59	1.63	229.8	0.053	44,000
4	Viton®-lined fish-paper	1/32	Inverted	3.52	1.64	237.4	0.121	25,000
2	Unlined fish-paper	1/16	Inverted	3.78	1.55	231.5	0.064	41,000
1	Unlined fish-paper	1/32	Inverted	2.60	1.57	164.5	0.060	40,700
4	2-Ply[b] paper-tape	--	Upright	4.07	1.62	125.9	0.057	41,700

[a]Composition - 52/26/22 - Mg /$NaNO_3$/XFS-4008L - EC-MA - DEGDN.
[b]1.25-inch diameter.

SECTION IV

SODIUM NITRATE PARTICLE SIZE EFFECTS

To conduct meaningful composition optimization and also achieve minimum binder levels, effective control of castability is necessary. Previous work had shown that the particle size of $NaNO_3$ has the greatest single effect on castability. It was found that screening dried Lee-Attrition milled $NaNO_3$ through 400 mesh immediately prior to use consistently produced the lowest viscosity. It is believed that $NaNO_3$ exhibits a great tendency to agglomerate or coalesce on storage, a phenomenon that is aggravated by atmospheric humidity.

It also was discovered that the anti-caking agents MgO and Cab-o-sil minimize the rate and extent of coalescence during storage. Therefore, all $NaNO_3$ used in this program contained 0.5 percent MgO and 0.25 percent Cab-o-sil.

A. MIKRO-PULVERIZER

Screening through 400 mesh is tedious and inefficient, and probably is unacceptable for large scale processing. Attempts proved successful to substitute a production type of grinder, the Mikro-Pulverizer, for the preparation of acceptably fine $NaNO_3$. Table V shows that while compositions employing unscreened Mikro-pulverized $NaNO_3$ may be slightly less efficient, burning rate and castability are favorably affected. Screening through 400 mesh appears unnecessary. This technique was adopted for all optimization studies. Anticake agents may be added prior to or after grinding.

In studies aimed at further particle size reduction, $NaNO_3$ with anticake agents was passed twice through the Mikro-pulverizer. This treatment diminished the castability.

Continuing efforts were made to lower binder content by reducing the particle size of $NaNO_3$ and eliminate as much as possible any aggregates. This led to a reevaluation, passing the Mikro-pulverized $NaNO_3$ through a 400-mesh screen in the RO-tap screening apparatus. More rapid screening was obtained, making this possibly an acceptable processing operation. The improvement is due to finer grinding by the Mikro-pulverizer and incorporation of anti-cake agents prior to grinding. Data in Table VI, gathered on 100-g mixes, indicate the relative merits of screening, and the possibility of achieving castable compositions at 19 to 20 percent binder.

B. SODIUM NITRATE DISPERSION

Because reagglomeration of the finely divided $NaNO_3$ occurs upon addition to hydrophobic binder systems, prewetting with surfactants was investigated for possible further reduction

TABLE V. PROCESSING $NaNO_3$

Batch Number	$NaNO_3$ Type	Batch Size (g)	Brookfield Viscosity (cps)	Luminous Efficiency (cd-sec/g)	Burning Rate (in/sec)
Composition A - 50.29/27.71/22.0 - Mg /$NaNO_3$ /XFS-4008L - EC-MA - DEGDN					
1942-86	Lee-Attrition (<400 mesh)	500	460,000	39,200	0.056
1942-89	Lee-Attrition (unscreened)	500	430,000	37,700	0.056
1942-87	Mikro-Pulverized 0.032" round hole screen (unscreened)	800	420,000	36,500	0.065
1942-91	Mikro-Pulverized 0.020" HB x 3/64B (unscreened)	800	180,000	36,600	0.062
Composition B - 52/26/22 - Mg/$NaNO_3$ /XFS-4008L - EC-MA - DEGDN					
1942-92	Mikro-Pulverized 0.020" HB x 3/64B	800	290,000	38,200	0.066
1942-95	Mikro-Pulverized 0.020" HB x 3/64B	8000	200,000	38,600	0.056

in binder levels. Prewetting $NaNO_3$ with non-ionic Tergitol E-35 proved most efficient, followed closely by non-ionic Dow surfactant 9N4. However, at surfactant/$NaNO_3$ concentrations of 10-15 percent, the quantity necessary for thoroughly wetting $NaNO_3$, there was evidence of incompatibility. Subsequent studies revealed that only 0.5 percent added to the binder reduced viscosity and improved castability consistently and effectively.

TABLE VI. EFFECT OF $NaNO_3$ PARTICLE SIZE ON VISCOSITY

Processing of $NaNO_3$	% Binder	Viscosity 25°C (cps)
Lee Attrition Mill Screened through 400 mesh	22.0	87,500
Mikro-Pulverized No screening	21.0	162,500
Mikro-Pulverized Screened through 270 mesh	21.0	125,000
Mikro-Pulverized Screened through 400 mesh	21.0	90,000
Mikro-Pulverized Screened through 400 mesh	19.0	400,000 to 600,000

Studies shown in Table VII, using the 50/30/20, - magnesium/$NaNO_3$/binder composition, demonstrate the effectiveness of viscosity reduction with Tergitol E-35.

TABLE VII. VISCOSITY REDUCTION WITH TERGITOL E-35[a]

Viscosity (cps)	Tergitol E-35 (%)
240,000	0
173,000	0.25
145,000	0.50
130,000	0.75
115,000	1.00

[a] 50/30/20 Mg/$NaNO_3$/XFS-4008L - EC-MA - DEGDN.

Because of time limitations, no surveillance stability data were obtained on surfactant-containing formulations. Therefore, surfactants were not utilized in the final optimized composition.

SECTION V

MAGNESIUM PARTICLE SIZE

Particle size variations in commercially available atomized magnesium are common. Earlier studies indicated that an excess of material finer than 100 mesh is undesirable and leads to high viscosity and poor castability at the desired low binder levels. It was recommended that the 40/200 grade magnesium contain a maximum of 15 percent finer than 100 mesh. However, studies with a recently obtained lot of magnesium (PO No. 034273) do not bear out this conclusion. Table VIII shows a screen analysis and resulting comparative viscosities of three 40/200 lots of magnesium.

TABLE VIII. MAGNESIUM PARTICLE SIZE DISTRIBUTION

Mesh No. % on	Lot No. 2097	Lot No. 033992	Lot No. PO 34273
60	31.1	15.1	50.2
80	24.6	31.1	38.3
100	32.2	11.6	6.5
140	4.3	23.0	4.4
200	4.0	16.8	0.3
230	3.0	1.5	0.1
Pan	2.0	--	0.1
Viscosity cps[a]	306,300	>1,000,000	750,000

[a] 50/30/20 Mg/$NaNO_3$/binder (XFS-4008L - EC/MA - DEGDN).

Both the coarser PO 34273 and finer 033992 lots lead to high mix viscosities. Because 2097 was in short supply, a study was undertaken to determine the most efficient magnesium particle size distribution for maximum castability by blending the above three lots. Furthermore, because 033992 contained a

broad distribution, it was separated into +100 and -100 mesh fractions to study particle size effects more easily.

The most efficient combination was a 50/50 blend of 2097 and +100 mesh 033992. However, the quantity of 2097 available was insufficient to prepare all the Air Force sample flare candles. It was found that a 65/25/10 ratio of +100 mesh 033992/2097/034273 produces a viscosity of 175,000 cps at 25°C, in a 50/30/20 - Mg/$NaNO_3$/binder composition. When 10 percent magnesium fines (<100 mesh 033992) was added, the data presented in Table IX were obtained. This shows the significant effect of this particle size distribution and of freshly screened $NaNO_3$ on viscosity.

TABLE IX. EFFECTS OF FRESHLY SCREENED $NaNO_3$ AND MAGNESIUM PARTICLE SIZE DISTRIBUTION

	Lot 2097	Blend
50% Magnesium	100%	58.5%, 033992, +100 mesh 22.5%, 2097 9.0%, 034273 10.0%, 033992, -100 mesh
30% $NaNO_3$	Mikro-pulverized	Mikro-pulverized freshly screened
20% Binder (XFS-4008L, EC-MA, DEGDN)	Same	Same
Viscosity, 25°C cps	306,000	185,000

Figure 1 shows the comparative particle size distribution of Lot 2097, the blend which gave minimum viscosity, and the blend shown in Table IX.

On the basis of these studies, it was decided to use the 58.5/22.5/9.0/10.0/magnesium blend and freshly screened Mikro-pulverized $NaNO_3$ for the preparation of sample candles for evaluation at the Air Force Armament Laboratory.

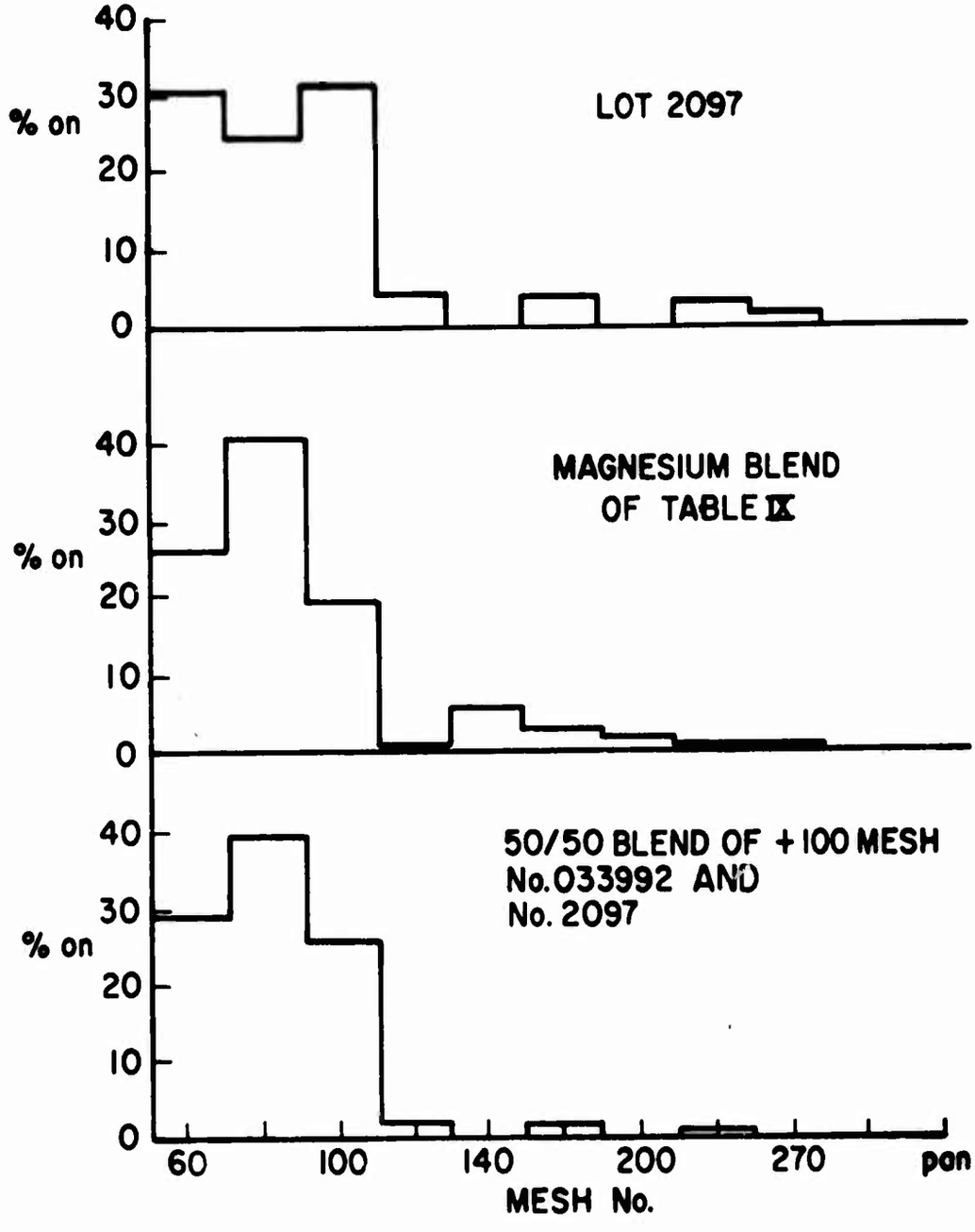

Figure 1. Particle Size Distribution of Magnesium Powders

SECTION VI

COMPOSITION OPTIMIZATION

The compositions shown in Table X result from a composition optimization, conducted in 3.4-inch I.D. Viton® lined paper-phenolic cases and fired in the inverted position.

At the 20-percent binder level about 50 to 52 percent Mg and 28 to 30 percent $NaNO_3$ appear to be optimum. The 50/30/20 composition was selected for the preparation of sample experimental candles for evaluation by the Air Force because of the higher luminous efficiency in the 3.4-inch diameter candle.

TABLE X. OPTIMIZATION, CAST CANDLES

Comp Number	Composition[a]	Viscosity (cps) 25°C	Burn Rate (in/sec)	Luminous Efficiency (cd-sec/g)
1942-112	52/28/20	275,000	0.061	42,600[b,c]
1942-113	50/30/20	306,000	0.059	45,000[b,c]
1942-117	48/32/20	537,500	0.057	38,400[b,c]
1942-109	52/28/20	275,000	0.066	53,000[d]
1942-110	50/30/20	306,000	0.060	50,800[d]
1942-117	48/32/20	537,500	0.057	37,800[d]
Mark 45 Comp			0.055	55,700[d]
Mark 45 Comp			0.055	53,200[d]

[a] Mg/$NaNO_3$/Binder: Magnesium Lot 2097, 40/200. $NaNO_3$ - Mikro-pulverized, 0.50% MgO and 0.25% Cab-o-sil, unscreened. Binder - KFS-4008L, 27.1%; EC/MA, 37.9%; DEGDN, 35%.

[b] Inverted firing.

[c] 3.4-inch diameter paper-phenolic case.

[d] 1.25-inch diameter paper-tape case.

SECTION VII

SAMPLE CANDLES

A. PRELIMINARY BATCH

A 5,000.0-g batch of composition 1942-110 (Table X) was prepared to study castability and combustion behavior. It contained the magnesium blend shown in Table IX and $NaNO_3$ freshly screened just prior to use.

A very favorable viscosity was obtained for this mix, 185,000 cps at 25°C. A lower binder level might be achieved, with better performance.

B. MARK 24 CANDLES

Mark 24 candles received from Eglin AFB were functioned for purposes of comparison with the best efforts cast flares. Most of these candles were fired in the inverted position. Several of the Mark 24's burned significantly faster than the nominal burning time of 180 ± 10 sec. Most of them broke up and fell to the floor near the end of functioning, the faster-burning ones sooner.

Table XI shows the results on these Mark 24 candles, along with comparative data on the best efforts cast candles. The lot number was undecipherable on many of the Mark 24 candles; it is recorded where available.

The average efficiency of all the Mark 24 candles fired was 27,900 cd-sec/g. If only those with burning times of 170 sec or greater are selected, the average is 29,100 cd-sec/g. The average of the latter group is 30,000 cd-sec/g for inverted firings and 27,400 cd-sec/g for upright attitude. In some firings smoke obscuration was evident. Because of the higher burning rate and greater diameter of the Mark 24 candles, it would be expected that smoke problems would be more severe than for the 3.4-inch cast flares.

The average efficiency for the best efforts cast candles was 40,650 cd-sec/g, 43,400 cd-sec/g for the inverted firings. The average burning rate was 0.057 in./sec. The average intensity was 570,000 cp, 640,000 cp for the inverted firings. These results are considered highly encouraging.

C. SAMPLES FOR AIR FORCE EVALUATION

Based upon these data, thirty 3.4-inch diameter flares were produced in four batches and shipped to Eglin AFB.

TABLE XI. MARK 24[a] AND CAST[b] CANDLES: COMPARATIVE FIRINGS

Candle	Burning		Efficiency	Intens	Attitude
	Time (sec)	Rate (ips)	(cd-sec/g)	(10^6 cp)	
Mark 24 (lot ?)	177	0.090	32,000	1.46	Inverted
Mark 24 (lot ?)	187	0.085	28,800	1.25	Inverted
Mark 24 (lot ?)	180	0.089	27,700	1.25	Inverted
Mark 24 (lot?)	176	0.091	27,000	1.24	Inverted
Mark 24 (lot 1429)	152	0.105	25,000	1.33	Inverted
Cast,80-1	82	0.057	42,800	0.63	Inverted
Mark 24 (lot 1429)	157	0.102	27,000	1.39	Inverted
Cast,80-2	80	0.059	43,800	0.66	Inverted
Mark 24 (lot ?)	197	0.082	34,000	1.40	Inverted
Cast,80-3	84	0.056	43,600	0.62	Inverted
Mark 24 (lot 1426)	147	0.109	23,900	1.32	Inverted
Mark 24 (lot 1429)	187	0.086	29,900	1.30	Upright
Cast,80-4	90	0.056	32,400	0.43	Upright
Mark 24 (lot 1426)	174	0.092	24,500	1.14	Upright
Mark 24 (lot ?)	182	0.080	27,900	1.30	Upright
Mark 24 (lot ?)	192	0.080	30,300	1.28	Inverted
Mark 24 (lot ?)	158	0.101	24,100	1.24	Inverted

[a] 4.25-inch diameter, cardboard case.

[b] 3.4-inch diameter, paper-phenolic case.

SECTION VIII

PROCESSABILITY

A. SCALING-UP

Successful scaling-up from 100 g to 400-600 g and then to 5000 to 8000 g batches was accomplished. The viscosities obtained in smaller batch sizes were maintained or improved. No mass effect on cure rate or exotherm was noted in the larger scaled-up batches, indicating adequate pot life at ambient temperatures, irrespective of batch size. Thus, production scale operation should present no difficulties.

B. CURE TEMPERATURE AND VIBRATION EFFECTS ON DENSITY

Because curing at a constant 70°C yielded some variations in flare densities, a study was undertaken to optimize curing conditions. Table XIII indicates that density decreases with higher temperature curing. However, maximum density was obtained with an initial low temperature cure, followed by a post-cure at 70°C. Presumably this contributes to degassing of the mix. In an effort to eliminate the two-temperature cure cycle, it was found that 1/2-hour exposure of cast flares to mechanical vibration produced similar or increased densities.

TABLE XII. EFFECT OF CURING TEMPERATURE ON DENSITY[a]

Composition Number	Curing Temperature (°C)	Density (g/cc)	Burning Rate (in/sec)	Luminous Efficiency[b] (cd-sec/g)
1942-92-1	46	1.60	0.061	44,500
1942-92-3	60	1.53	0.064	43,100
1942-92-5	70	1.47	0.072	45,200
1942-95-7	45-70	1.69	0.056	44,800
Mark 45 Composition	70	1.70	0.060	51,200

[a] Composition - 52/26/22 - Magnesium/$NaNO_3$/Binder (XFS-4008L - EC-MA - DEGDN).

[b] 1.25-inch diameter tape-wrapped candles.

C. HAZARDS STUDY

The final mix temperature of 24.5°C in an 8,000 g mix indicated a safe minimal exotherm on mixing. In a curing exotherm test, a 3.4-inch diameter by 4-inch long cast flare displayed a mild and easily controllable exotherm of 7.0°C for approximately 15 to 20 minutes.

A DTA trace of an uncured mix is shown in Figure 2. It exhibits no exotherm until above 150°C and an ignition temperature above 300°C.

Using the Olin drop weight tester, the impact sensitivity, E_{50}, was found to be 280 Kg-cm.

In standard explosive booster tests, using 10 g of C-4 and a No. 6 blasting cap, no detonation could be propagated. This test was done on a 117 g 1.25-inch diameter candle in a paper-phenolic case, a 232 g 1.7-inch diameter candle in a fish-paper case, and an approximately 260 g 1.85-inch diameter candle with no case.

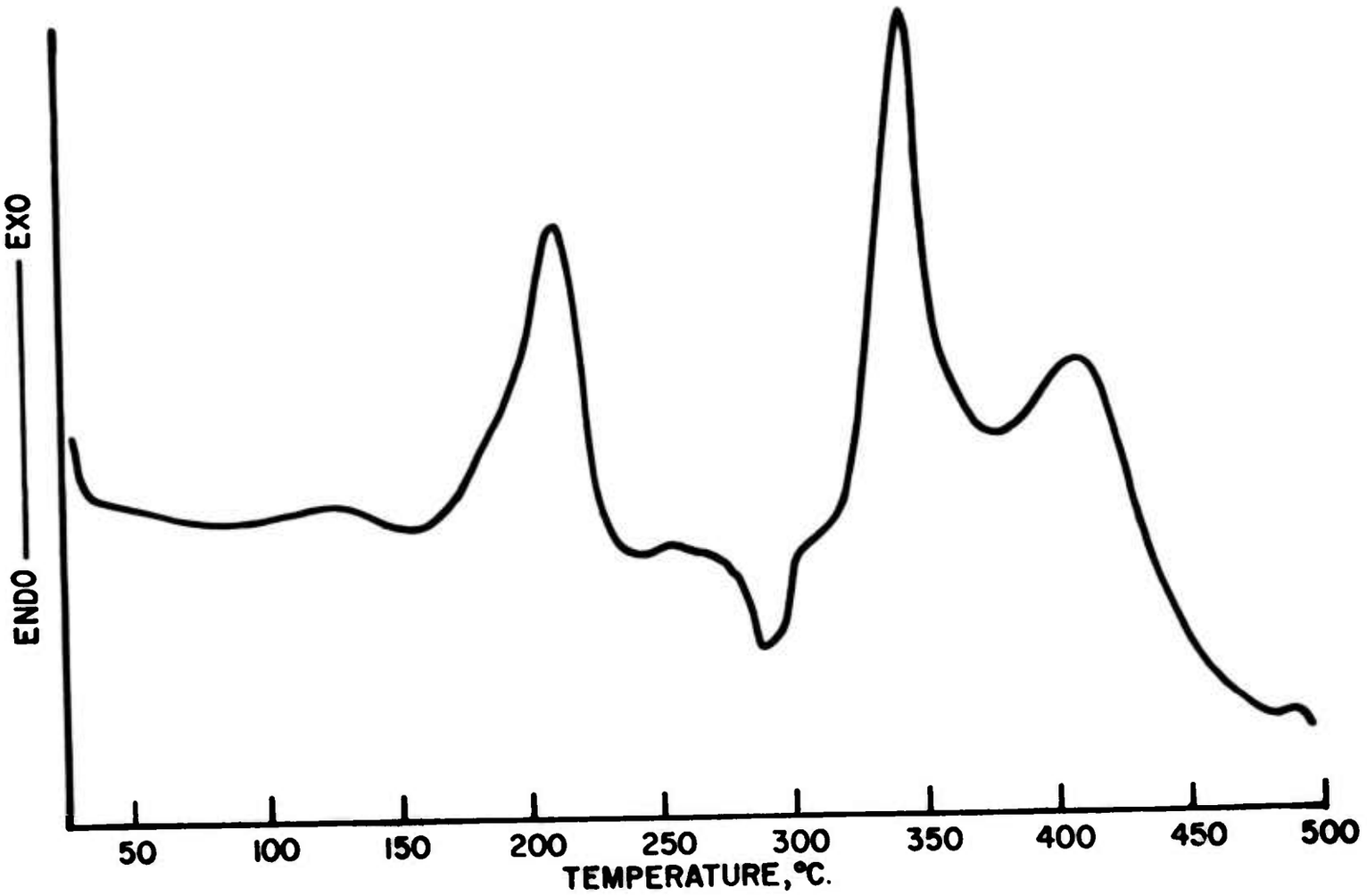

Figure 2. Differential Thermal Analysis of Best Efforts Mix

SECTION IX

NEW BINDERS

A. POLYESTERS

Several experiments used oxygen-rich vinyl esters formed from unsaturated olefins. Resins were studied of ethylene glycol (EG) (52 percent oxgyen) and MA (49 percent); hydroxyethyl acrylate (HEA) (41 percent oxygen) and MA; and HEA, MA, and allyl diglycol carbonate (ADGC) for crosslinking purposes. These appeared promising in neat binder studies, but complete compositions displayed high exotherms, gassing, and decomposition during mixing and curing. Reaction of Mg with carboxyl groups in the presence of water of esterification was presumed responsible.

A more promising system was homopolymerized ADGC or its copolymer with MA. Flare compositions based on this binder seemed compatible, and relatively high oxygen content (42 to 44 percent) was attainable. Of even more interest was Dow experimental material Tex-R-1939, the diacrylate of bishydroxyethyl carbonate (43.5 percent oxygen).

B. TEX-R-1939

1. Investigatory Studies

Because Tex-R-1939, when used as a primary binder component, displays excellent wetting qualities, good pot life, a high level of compatibility, and rapid cure rate at elevated temperatures, considerable effort was directed toward its development.

Free radical initiators MEK peroxide, cumene hydroperoxide, and lauroyl peroxide were found to catalyze homopolymerization of Tex-R-1939 efficiently. A 0.3 percent concentration of lauroyl peroxide is recommended for curing at 70°C.

Initial studies of unplasticized 10-g mixes indicated that a 1:1 mole ratio of Tex-R-1939 to MA, with EC added in a quantity equal to the MA (for higher oxygen content), resulted in a promising composition containing 24 percent binder. The viscosity was very low (<100,000 cps, at 25°C), and the polymerization rate and exotherm were easily controllable. Grain integrity appeared excellent with no evidence of expansion or doming during cure. However, subsequent studies with larger mixes gave low luminous efficiency. For example, at 17.4 percent binder, with no nitrate ester plasticizer, approximately 34,000 cd-sec/g efficiency was obtained at a burn rate of 0.070 in./sec. Attempts to increase oxygen content by incorporating tartaric acid (64 percent oxygen) proved detrimental to grain integrity. Co-curing with XFS-4008L

for increased cross-link density also failed to improve luminous efficiency. The same was true of allyloxypropyl glycidyl ether, (AOPG) when copolymerized with Tex-R-1939 and MA.

Since it appeared that an acceptable efficiency level could not be reached without a nitrate ester plasticizer, work was begun on TEGDN plasticization of a homopolymerized Tex-R-1939 binder. These compositions produced excellent viscosities, ranging from 37,500 to 55,000 cps at 25°C with TEGDN levels of 0 to 40 percent of the binder. Interestingly, all the candles containing TEGDN, even 40 percent TEGDN, displayed very dry surfaces, indicative of the high plasticizer tolerance capacity of Tex-R-1939. An efficiency of 38,300 cd-sec/g was obtained with 40 percent TEGDN plasticizer content. Additional studies, shown in Table XIV, revealed that 47,000 cd-sec/g, luminous efficiency and favorable burning rates can be achieved with 40 to 50 percent TEGDN or DEGDN levels. Initial data indicate that the 52/28 ratio is an approximate optimum for the $Mg/NaNO_3$ ratio.

TABLE XIII. COMPOSITIONS CONTAINING TEX-R-1939

Ingredient	Percent Composition				
Mg	49.0	52.0	49.0	52.0	52.0
$NaNO_3$	27.0	28.0	31.0	28.0	28.0
Tex-R-1939	14.4	12.0	12.0	10.0	10.0
TEGDN	9.6	8.0	8.0	10.0	--
DEGDN	--	--	--	--	10.0
Lauroyl Peroxide	0.2	0.2	0.2	0.2	0.2
Binder	24.0	20.0	20.0	20.0	20.0
Plasticizer in Binder	40.0	40.0	40.0	50.0	50.0
	Performance				
Viscosity, cps 25°C	52,500	500,000	220,000	245,000	265,000
Burn Rate, in/sec	--	0.067	0.064	0.071	0.082
Luminous Efficiency, cd-sec/g	38,300	45,000	38,200	45,200	46,800

2. Surveillance

These compositions show a slight surface softness at the 50 percent plasticizer level, possibly indicating over-plasticization. A duplicate 500-g batch prepared for surveillance studies (Table XV) gave no indication of migration or incompatibility at a slightly higher (0.30 percent) catalyst content. Thus it appears that more than 50 percent DEGDN or TEGDN could be tolerated. These surveillance data reveal that a composition based on Tex-R-1939 - DEGDN binder shows promising surveillance stability. Weight loss is acceptably low. Combustion data (representing only one candle) show varying luminous efficiency values. It is believed that this reflects observed varying chimney effects and side burning, rather than composition degradation.

TABLE XIV. SURVEILLANCE OF TEX-R-1939 - DEGDN BASED COMPOSITION[a]

Parameter	Days at 70°C			
	0	10	24	31
Weight Loss, %	--	0.18	0.17	0.14
Color and Integrity	--	No Change		
Plasticizer Exudation	--	None Detected		
Ignition		Immediate		
Lum Eff, cd-sec/g[b]	40,600	36,200	26,700	31,650
Burn Rate, in/sec[b]	0.082	0.077	0.084	0.082

[a]Magnesium, 51.6%; $NaNO_3$, 28.4%; Tex-R-1939, 10.0%; DEGDN, 10.0%.

[b]Single candles.

Safety tests showed an impact sensitivity (E_{50}) of 280 kg cm for the composition with 20 percent TEGDN in the binder. At 30 and 40 percent TEGDN, values of 251.0 and 218.0 Kg cm were obtained, respectively. It can be predicted that (E_{50}) for the 50 percent TEGDN composition will fall in the range of 150 to 200 Kg cm.

3. Other Additives

The curing agents D.E.H.®[1] 20 (diethylenetriamine, DETA) and ethylenediamine (EDA) were investigated at low binder level in Tex-R-1939 compositions, because of their ability to solubilize $NaNO_3$. A very rapid exothermic cure was obtained, indicative of amine-double bond copolymerization with Tex-R-1939.

The plasticizer DEO (diethyl oxalate) was studied in an attempt to confirm a promising data point obtained during an earlier program. It was found to give poor luminous efficiency in compositions containing XFS-4008L - MA and XFS-4008L - EC-MA binders. Therefore, work was not pursued in Tex-R-1939 binder systems.

Substitution of the reactive diluent allyl glycidyl ether (AGE) for DEGDN in a Tex-R-1939 - D.E.H.® 24 binder system yielded castability at 17.5 percent binder level. However, combustion properties were very poor.

Substitution of Dowanol®[2] EM (ethylene glycol methyl ether), a $NaNO_3$ solvent, for DEGDN in the XFS-4008L - EC-MA - DEGDN binder system resulted in incompatibility. However, it proved compatible in diamine cured epoxy systems. A first attempt resulted in a castable mix at 15 percent XFS-4008L - AGE - D.E.H.® 24 - Dowanol®EM binder, using 30/50 magnesium.

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[1]D.E.H., a trademark of The Dow Chemical Company for epoxy curing agents.

[2]Dowanol, a trademark of The Dow Chemical Company for glycol ethers.

SECTION X

CONCLUSIONS AND RECOMMENDATIONS

The best efforts cast candles in 3.4-inch paper phenolic cases give very promising performance. They are superior in efficiency to the Mark 24 candles tested, although it is felt the latter suffered from poor reproducibility, case bond failure, and tunnel smoke problems. In 1.25-inch taped cases, the best efforts cast composition is nearly equivalent to the Mark 45 composition. Thirty 3.4-inch flow-cast candles have been furnished to Eglin AFB. Results obtained from firing these items will give a better comparison of the flow-cast candles with standard pressed candles.

No surveillance work has been done on 3.4-inch cast candles in paper-phenolic cases. It is recommended that some of the sample candles supplied to Eglin AFB be stored at 70°C for 1 to 4 weeks and then functioned.

Results on 1.25-inch fish-paper cases were encouraging. Cast 3.4-inch candles should be tested in these cases.

It was shown that mix viscosity can be reduced by employing surfactants. Since no time was available for surveillance of such a composition, however, it was not used in the best efforts flares. A 28-day storage test at 70°C should be performed. If these candles prove stable, further optimization work should be done on the low viscosity mix. Binder level can be reduced to the limit of castability. The $Mg/NaNO_3$ ratio should then be readjusted to maximize efficiency within the constraints of flow castability.

Considerable work was done on Mg particle size distribution during this program. However, the acceptable limits on this parameter have not been established fully. This type of effort is time-consuming, but it should be pursued.

Two polyester binders studied during this program merit further effort. A minimum of work was done on ADGC and ADGC with MA or EC-MA. This research should be carried forward. Compositions based on Tex-R-1939 appear very desirable. High temperature surveillance tests should be run on compositions with Tex-R-1939 binders plasticized with DEGDN and with TEGDN . This type of composition should be scaled to 3.4-inch candles and the composition optimized. As a part of this program, a sample of Tex-R-1939 has been supplied to Eglin AFB for further formulation work.

Because of the promise of flow-cast compositions shown during this program, flow-cast mixes should be considered for any new illumination items and as an alternate for current flares.

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13. ABSTRACT

Previous work (Contract F08635-70-C-0028, Eglin Air Force Base) gave encouraging results for flow-cast illumination flares. The present development effort has resulted in compositions comparable in performance with pressed mixtures. Viton®-lined paper phenolic cases have proved satisfactory in 3.4-inch-diameter size. The agglomeration of sodium nitrate can be reduced by the addition of MgO and Cab-O-sil. However, the oxidizer also should be used immediately after grinding to avoid agglomeration. Surfactants can be used to improve mix viscosity. The particle size distribution of magnesium used is critical to mix viscosity and luminous efficiency. With 20 percent binder in the mix, maximum performance is obtained at about 52 percent Mg for 1.25-inch candles and 50 percent Mg for 3.4-inch candles. The best efforts formulation contains 50 percent of a 40/200 mesh Mg blend, 30 percent $NaNO_3$, and 20 percent of XFS-4008L - EC-MA - DEGDN binder. In 3.4-inch candles it yields 43 to 45,000 cd-sec/g efficiency at 0.056-0.059 in./sec burning rate. This mix has been scaled up to 10-kg batch size. Further work has also been accomplished on new binders. The most promising is based on a vinyl ester, Tex-R-1939, plasticized with DEGDN.

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Castable pyrotechnics						
Flow casting						
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